COORONGITE, BALKASHITE AND RELATED SUBSTANCES—AN ANNOTATED BIBLIOGRAPHY

by R. F. CANE*

Summary

CANE, R. F. (1977) Coorongite, balkashite and related substances—an annotated bibliography. *Trans. R. Soc. S. Aust.* 101(6), 153-164, 31 August, 1977.

A resurgence of interest in coorongite has been occasioned by the search for renewable hydrocarbon energy sources. Coorongite is a biogenic polymer originating in profuse blooms of an aberrant alga, *Botryococcus braunii* (Kutzing). *B. braunii* can exist in three physiological states, two of which produce large quantities of polyene hydrocarbons. On the death of the colony, the hydrocarbon metabolites oxidize and polymerize into a dark coloured rubbery mass, called coorongite, from which a hydrocarbon oil can be obtained by pyrolysis.

The lack of a comprehensive bibliography on coorongite and related bio-elaterites has been felt by workers in this field. The present survey, which covers the period 1866-1976, makes good this deficiency.

Introduction

For more than a century it has been recognised that algae provide useful information on the genesis of petroleum. Increasing appreciation of this fact, together with advances in the techniques of analytical chemistry, has resulted in the chemistry of algae becoming an important study for organic geochemists. One outcome of these researches has been a much better knowledge of the geochemical processes which occur during the diagenesis of earth hydrocarbons.

In addition to biologically derived liquid petroleum, there are other types of hydrocarbon deposit which have received recent attention. These may be arranged into three groups, namely:

(i) material resulting from the alteration of petroleum to yield brittle, largely insoluble solids such as wurtzilite, grahamite and gilsonite;
(ii) abiotic hydrocarbons;
(iii) polymeric hydrocarbons arising from extant algae.

The purpose of this paper is to review the literature of the polymeric group and to present a bibliography of an important South Australian representative called coorongite.

Coorongite is a naturally occurring rubbery polymer arising from a specific alga and, like balkashite from Kazakh (Siberia), has its genesis in prodigious blooms of an atypical colonial alga, *Botryococcus braunii*. There are only three known representatives of this type of substance, all of which are of the same algal origin and, presumably, have the same chemical composition, but only coorongite has been fully examined. These representatives and their main habitats are:

(i) Coorongite—The Coorong (South Australia);
(ii) Balkashite—Lake Balkash (Siberia);
(iii) N'Hangellite—Lake N'Hangella (East Africa).

There are dubious reports of other occurrences but these have not been authenticated.

Until a decade ago, the problem of the chemical composition of coorongite had received only scant attention because it had been tacitly assumed that the work of Stadnikov (1929 *et seq*) and others had established the nature of the "algal oil". The availability of gas chromatography and computerized mass spectrometry has now shown that the previous assumptions were wrong and, over the last few years, there have been important publications on this topic. As recently as 1976, it has been suggested (Hillen 1976) that the alga should be fully investigated as a possible future source of hydrocarbon energy.

* Queensland Institute of Technology, Brisbane, Qld 4000.

Because of the present interest in hydrocarbon-producing algae, it was decided to collect together all reliable information on the nature of coorongite and related materials, with particular refence to the role of *B. braunii* in the formation of such bio-elaterites. It is inevitable that some citations will provide only passing reference but, for completeness, such material has been included. References dealing with *Botryococcus* purely from the viewpoint of taxonomy or algology have been excluded unless the text has some direct bearing on coorongite and its allies.

History of Coorongite

Although coorongite was reported in 1852 (see Scrutton 1874—Suppl.), the first description was that given by Francis (1866—Suppl.), followed by an initial scientific report by Dyer (1872). Prior to these dates, the only interest in coorongite (balkashite) had been as a source of fuel by the Khugese tribe of Turkeston (Morgan 1921). Some aboriginal tribes of South Australia had occasionally burned coorongite to provide light.

Because of the appearance of coorongite and its burning characteristics, Dyer (1872) believed that it might be of mineral origin and hence indicate the presence of underlying mineral oil. Arguments over the origin of coorongite were to extend over the next half century (Colyer 1974). If of mineral origin, it was argued, it was likely that "millions of tons" of petroleum was underlying the Coorong. If it were a vegetal growth, it could be grown to produce much oil, so it was said. Early chemical analyses showed that the pyrolysate of coorongite was largely unsaponifiable. This information was used by the "mineral oil" protagonists as evidence of the relation of coorongite to petroleum. More reliable work by Boodle (1907) and later by Cuming (1902) showed that samples of coorongite did contain appreciable saponifiable matter and the field observations of Broughton (1920) left no doubt of the vegetal origin of coorongite and of its mode of formation.

After the establishment of the origin of coorongite, the assumption that the "algal" oil was fatty ester remained the consensus for nearly half a century. Scientific opinion was strengthened by the comprehensive botanical papers of Blackburn (1936) and Temperley (1936), and the extensive organic geochemical studies of Stadnikov & Weizmann (1929) and Stadnikov (1930). In order to provide a suitable model for his studies of the origin of coorongite and torbanite, Cane (1967) used elaeostearic acid for the synthesis of "synthetic" coorongite, basing his premise on the assumption that the decarboxylated dimer ($C_{34}H_{58}$) was the main "building block". His hypothesis was reasonably satisfactory but there were still unexplained features. Later, Maxwell *et al.* (1968) using computerized mass spectrometry, showed that the algal lipid matter (of the orange form of the alga) was not fatty ester, as previously supposed, but two isomeric polyene hydrocarbons ($C_{34}H_{58}$) which they called botryococcene and isobotryococcene. At that stage it seemed obvious that botryococcene polymer was the matrix of coorongite. Further work by Cane & Albion (1973) led to the conclusion that coorongite originated, not from the botryococcenes, but from alkadiene hydrocarbons produced from the green form of the alga although botryococcene has a small but still important role. Later work has shown that the nature of coorongite varies more widely than previously supposed and that the composition can be dependent on the ecological conditions during formation. Post-depositional changes are also important. Nevertheless, it is now clearly established that coorongite is essentially a hydrocarbon polymer arising directly by algal metabolism.

The nature of Botryococcus braunii

Botryococcus braunii is an ubiquitous alga distributed from the tropical to temperate climates in many parts of the world. As well as having a wide geographical occurrence, *B. braunii* occurs, as fossil forms, in many geological eras as far back as the Ordovician, indeed, as Dulhunty (1944) writes "that organic evolution should have allowed the organism to remain unchanged over the immense length of time since the Permian coal measures were laid down, is extraordinary". The alga also occurs in a fossilised condition in the Kukkersite oil shale of Estonia, and as the main contributor to the torbanites of New South Wales, Scotland and South Africa. Fossil *B. braunii* has been found in English and American peats, in the mud of glacial lakes, in carbonaceous clays, and in some recent carbonate rocks. In extant form it is usually found in fresh-water areas ranging in size from small ponds to lakes although it can also be found in brackish swamps, bogs and even in salt water. Under, as yet, undefined conditions, *B. braunii* "blooms" to yield large areas of a floating mass of colonies which, on drying at shore lines, have been reported as being of hundred of square metres in extent and up to several centimetres thick. The dried material after some oxidation and ageing is called coorongite.

The ubiquity of *B. braunii* has given rise to some confusion because algologists at various places have not recognised the genus with which they were working. Thus, the species has been "rediscovered" under the generic names of *Pila*, *Reinschia* and *Elaeophyton*. The family affiliation of the genus has also been controversial, however, the work of Belcher & Fogg (1955) using phytochemical criteria, has placed the genus unequivocally in the *Chlorophyceae*.

Botryococcus braunii exists in three distinct growth states (Belcher (1968). Brown, Knights & Conway (1969)), each with quite different lipid composition. The three states are:

(a) a green coloured, thin cell-walled rapid growth stage. The hydrocarbon metabolite consists of about 30% of straight chain C_{27}-C_{31} dienes;

(b) an orange coloured thick walled resting stage. The hydrocarbons are largely branched chain C_{34} polyenes.

Both forms are colonial, and

(c) a single celled dark green dormant variety containing little hydrocarbons.

The morphology of *B. braunii* has been well documented, the classical contribution being the collaborative papers by Blackburn (1936) and Temperly (1936). These authors showed, beyond doubt, that torbanite and boghead coals had a common origin in vast growths of this alga and that the lipid matter of the algal cups provided the monomer for the organic matter of the minerals. The first instance of the recognition of *B. braunii* as the oil forming alga of these rocks was by Zalessky (1926), although, earlier, he had believed the alga belonged to the genus *Pila* (Zalessky 1914). Zalessky's research was mainly concerned with the identification of the organic matter of Estonian oil shale and like others, later, he recognised that balkashite (coorongite) was the "peat stage" in the diagenesis of algal organic rocks. Both Zalessky (1926) and Stadnikov (1930) believed that the "oil" of this alga was fatty matter and this opinion remained unchallenged until Maxwell's (1968) work in the last decade.

Utilization of Coorongite

It was mentioned in the Introduction that the burning of coorongite has been used by primitive people as a source of heat and light. The substance burns very readily and it has been stated that the infrequent and sporadic finding of coorongite is caused by the destruction of previous deposits by bushfires. In early newspapers, one reads of layers of coorongite ash many inches thick (there may be an element of imagination in this).

After the establishment of the origin of coorongite and the death of the "mineral oil" theory, from time to time it has been suggested that this material might provide a renewable source of energy in the form of liquid or solid fuel. The cultivation of the alga was suggested by Basedow (1925—Suppl.) and Sir Douglas Mawson is believed to have put forward a scheme at the 17th ANZAAS Congress in Adelaide. At the 47th ANZAAS meeting in Hobart, Hillen (1976) presented a case for the further study of *E. braunii* as a renewable hydrocarbon source and a potential fuel supply.

Bibliography

The bibliography has been compiled from first-hand study of all references except one of Zalessky's papers. In general, the verbal tense of the abstract is the present, except where the past tense more suits the original publication.

A BIBLIOGRAPHY OF COORONGITE AND COGNATE SUBSTANCES

containing abstracts of papers and occasional notes

BELCHER, J. H. (1968) Notes on the Physiology of *Botryococcus braunii* (Kutzing). *Arch. Mikrobiol.* **61**, 335-346.

A study on the growth of *Botryococcus* under varying conditions. The rate of early growth is exponential and the green colonies are heavier than water. After a few weeks a stationary phase is reached at which the colonies are red and floating; when subcultured, they revert to the green phase. Under non-bloom conditions growth is slow and large irregular colonies are formed. The paper discusses the effect of the environment on the chemical composition of the alga. The rubbery substance found in lakes in Australia, Africa and Siberia is a by-product of this alga. These deposits remain on the edge of lakes and are the result of hydrocarbon residues left behind on the death of the organism.

BELCHER, J. H. & FOGG, G. E. (1955) Biochemical Evidence of the Affinities of *Botryococcus*. *New Phytol.* **54**(1), 81-83.

The paper points out the uncertainties in assigning the taxonomic position of *Botryococcus*. Extracts of *B. braunii* were chromatographed and the eluents examined spectrographically. The absorption spectra and other phytochemical criteria show "clearly that the genus showed be placed in the *Chlorophyceae*".

BLACKBURN, K. B. (1936) *Botryococcus* and the Algal Coals. Part I—A reinvestigation of the alga *Botryococcus braunii* (Kutzing). *Trans. R. Soc. Edin.* **58**(3), 841-854.

This is Part I of the classical paper dealing with the role of *Botryococcus* in the formation of balkashite, coorongite and boghead coals. This paper traces the confusion of early workers regarding the taxonomy of the genus and notes how these misconceptions lead to misnomers. The algal morphology is treated in some detail including a discussion on the cell anatomy. Comment is made that the lipids of coorongite are very unstable and that widely different analytical results may be obtained depending on the age of the sample. The material of the cell wall is chemically highly unsaturated but, on exposure to air, the lipid matter becomes more inert and insoluble. This very thorough paper laid the groundwork in this field for the next three decades.

BOODLE, L. A. (1907) N'Hangellite and Coorongite. *Bull. Misc. Inf. R. bot. Gdns Kew* **5**, 146-151.

A description of the occurrence and nature of a gelatinous deposit found near Lake N'hangella in East Africa. Examination of specimens showed conclusively that the rubbery material originated in algal growth. It was suggested that the alga belonged "almost certainly to the blue green algae". Although chemical data are not given, a separate description and examination of coorongite (based partially on Dyer's observations) left no doubt that both coorongite and n'hangellite had a common origin and diagenesis.

Boodle expresses indecision as to how the "mucilage" of the alga became transformed into "material showing the characters of bitumen" but assumes extensive chemical change with loss of oxygen. He notes that n'hangellite is directly comparable to certain organic minerals and mentions a likely connection with the kerosene shales (of N.S.W.).

BROUGHTON, A. C. (1920) Coorongite. *Trans. R. Soc. S. Aust.* **44**, 386.

This short note occurs in "Miscellania" and consists of only two paragraphs. The note provides a first-hand description, one of the few, of the actual formation of coorongite from the green alga in The Coorong. In view of the uniqueness of this information, portions of the submission are quoted verbatim: "a thick scum, like green paint, is forming. This scum is drying on the water in places to a semi-elastic substance, forming around reeds . . . Like green paint, a quarter of an inch thick, it covers hundreds of square yards of water, and as it drys it forms a skin like linseed oil drying on an overturned mass of paint. This skin in places is yards in area."
"Today it is there in thousands of gallons. It is coorongite in process of formation . . . Every stage from the green, liquid, paint-like substance to the tough, elastic, sand-containing coorongite may be observed. Scooped with the hand from the surface of the lake this substance, within a few minutes, changes before the eyes from a green liquid, which drops from the fingers, to a brown, plastic solid. Large areas are now drying in sheets of coorongite."

BROWN, A. C., KNIGHTS, B. A. & CONWAY, E. (1969) Hydrocarbon Content and its Relationship to Physiological State in the Green Alga, *Botryococcus braunii*. *Phytochem.* **8**, 543-547.

Botryococcus is a peculiar alga characterised by the production of hydrocarbons which vary in composition with its three physiological states. The green active-growth form contains three homologous series of alkadienes in the C_{27}-C_{31} range, substantially of straight chain configuration with the general formula C_nH_{2n-2} where n = 27, 29, and 31. There is a second series, C_nH_{2n-4}, where, largely, n = 29.
The brown resting stage contains large amounts of highly unsaturated botryococcenes, which may be up to 86% of the dry weight of the colony. The dark-green large cell final stage has little hydrocarbon content. The chemical interrelationship of the stages is uncertain as the botryococcene producing stage reverts to diene production when subcultured. The paper establishes the main chemistry of each stage and shows that the hydrocarbon content varies with growing conditions.

BROWN, H. Y. L. (1908) *Rec. Mines S. Aust.* **4**, 350-351.

This annual report contains a short review on the occurrence of coorongite and the presence of mineral oil. It records that coorongite "is

an indiarubber material" found near Salt Creek which empties into The Coorong. After an examination of two bores in the area, the Government Geologist dismisses any likelihood of petroleum being found in the Coorong area.

BURGESS, J. D. (1975) *Botryococcus* Occurrence as an Aid in interpreting Paleoenvironments. Abstract only in *Geosci. Man* **11**, 154.

The full paper is a useful study of the morphology of *Botryococcus* as an indicator in determining the water environment during sedimentation processes. The occurrence of coorongite is discussed in the light of likely environmental conditions during the bloom stages. It appears that the main criterion in determining whether the thin wall or the thick wall stage is predominant is whether the alga is inhabiting fresh or brackish waters.

CANE, R. F. (1967) The Constitution and Synthesis of Oil Shale. Proc. 7th World Petrol. Congr. (Mexico) 3, 681-689 (Elsevier: Barking).

Although this paper is concerned with the origin of oil shale kerogen, the sections entitled "The Nature of Coorongite" and "Polymerisation of Fatty Oils" describe the likely reactions leading to the formation of coorongite. Coorongite analyses and its infrared spectrum are published. The important contribution made by this paper was the hypothesis that the coorongite (and kerogen) unit was a $C_{34}H_{58}$ polyene hydrocarbon. This unit was believed to be a dimer of a decarboxylated trienoic C_{18} acid. Later work showed that coorongite arises directly from algal hydrocarbons and not from an acid alkyl chain. The $C_{34}H_{58}$ molecule corresponds exactly to the same elemental composition as the dimer postulated in this paper.

CANE, R. F. (1969) Coorongite and the Genesis of Oil Shale. *Geochim. cosmochim. Acta* **33**, 257-265.

The history and occurrence of coorongite are reviewed. A theory is put forward that coorongite consists largely of a polymer of "hydrocarbon chains containing some unsaturation". Carboxylic groups occur at chain terminations and the non-polar end of the hydrocarbon chain appears to contain a diene structure. Ether cross-linkages are an important feature of the macromolecule. The molecular weight of the monomer (or the dimer) is about 430. Coorongite mass spectra showed a range of aliphatics. Alkaline permanganate oxidation produced a waxy solid with properties corresponding to fatty acids of high molecular weight.

CANE, R. F. & ALBION, P. R. (1971) The Phytochemical History of Torbanites. *Proc. R. Soc. N.S.W.* **104**, 31-37.

The paper shows that the phytochemistry of *Botryococcus* leads to an explanation of the formation of coorongite. The alga is exceptional in that it produces large quantities of unsaturated hydrocarbons which can be either branched or straight chain, depending on the physiological state. This state appears to depend on food reserves and environmental conditions. Coorongite undoubtedly arises from the polymerisation and oxidation of algal hydrocarbons. Spectral studies leave considerable doubt as to the number of methyl groups attached to the carbon chain "back bone" of coorongite. Some alkyl aromatic structures seem to occur in coorongite in addition to hydroxyl and carbonyl groups.

CANE, R. F. & ALBION, P. R. (1973) The Organic Geochemistry of Torbanite Precursors. *Geochim. cosmochim. Acta* **37**, 1543-1549.

This paper extends the work of Cane who had suggested that the building block of coorongite was a decarboxylated polyene acid corresponding to $C_{34}H_{58}$. Recent research had shown that the alga produces $C_{34}H_{58}$ directly and not from carboxylic acid. Further work, using mathematically derived data from proton resonance spectra indicates that long chain dienes from the green form of *Botryococcus* are the precursors to coorongite rather than the highly branched botryococcenes. The orange form of *Botryococcus* produces botryococcenes and these, in turn, form "botryococcus rubber" but not coorongite. The opinion is put forward that, in the field, there may be some contribution from branched chain hydrocarbons as well as carboxylic acids. Post-depositional microbial transformations also occur.

CARNE, J. E. (1903) The Kerosene Shale Deposits of N.S.W. *Mem. geol. Surv. N.S.W.*, 333.

This monograph is devoted to an exhaustive study of the occurrence and nature of the N.S.W. oil shales. The author quotes earlier opinions that there is no real evidence of flow oil in The Coorong. Reference is made to coorongite (p. 109 and p. 302) in connection with other possible oil sources in Australia. There is little additional pertinent information.

COLYER, F. (1974) Fools Gold. *Petrol. Gaz., Melb.* **18**, 58-63.

The text provides no scientific information but the general historical survey is of much interest. The article gives the history of

coorongite from its discovery in 1852. The paper traces the vicissitudes in belief of the interconnection between coorongite and flow oil and the endeavours of early entrepeneurs to raise share capital to drill for oil. Mention is made of previous ideas regarding the cultivation of algae as oil producers.

CONACHER, H. R. J. (1938) Coorongite and its Occurrence. *In* A. E. Dunstan (Ed.) *"Oil Shale and Cannel Coal"*, 42-49 (Institute of Petroleum; London).

The writer reviews the literature, pointing out that, because of the sporadic occurrence of coorongite, definitive information on the occurrence of deposits is lacking. Conacher visited The Coorong in 1935 and, although he was unsuccessful in observing coorongite in the natural state, he provides a very good description of its habitat. The article points out that coorongite is also found in Western Australia and discusses the environmental conditions which appear to favour the growth of the alga.

COX, R. E., BURLINGAME, A. L., WILSON, D. M., EGLINTON, G., & MAXWELL, J. R. (1973) Botryococcene—a Tetramethylated Acyclic Triterpenoid of Algal Origin. *J. Chem. Soc.* **D**, 284-285.

As a result of the use of ^{13}C nuclear mass resonance spectroscopy, with pulsed Fourier transform operation, a structural formula of botryococcene is suggested. It appears that botryococcene contains eight methyl, eight saturated and five unsaturated methylene, five saturated and three unsaturated methine carbon atoms. One saturated and four unsaturated quaternary carbons were also identified.

CUMING, A. C. (1902) Coorongite—A South Australian Elaterite. *Proc. R. Soc. Vict.* **15**, (n.s.) (2), 134-140.

The paper gives a general description of coorongite and provides references to its early history and discovery. Cuming's investigations showed that this substance could be separated into two portions depending on solubility in carbon bisulphide. The soluble portion was a wax-like solid, from the general properties and chemical analysis of which the formula $(C_{10}H_{18}O)_x$, with x about 8, was assigned. The insoluble portion, amounting to about three-quarters of the sample, was given the elemental formula $C_{10}H_{20}O_3$. As the solubles were readily oxidised, Cuming suggested (quite correctly) that the soluble portion may become insoluble by the combined effects of ageing and oxidation. Ash analysis showed that coorongite was not of animal origin.

CUMING, A. C. (1903) Coorongite, A South Australian Elaterite. *Chem. News* (London) **87**, 306-308.

A recast of the previous reference in an abbreviated form.

DAVID, T. W. E. (1890) Note on the Origin of "Kerosene" Shale. *Proc. Linn. Soc. N.S.W.* **4**(2), 483-500.

This paper, devoted to the origin of the torbanites of N.S.W. mentions the coorongite theory of biogenesis of oil shale. This is a most important paper as in it David initiates his algal theory of origin of oil shales. Microscopical evidence on the origin of coorongite strongly points to a vegetative source but David leaves the matter undecided. He points out that, if allowance is made for the elimination of oxygen, there are some striking points of resemblance between the chemistry of coorongite and the "kerosene" oil shales of Australia. The coorongite studies represent only a small portion of the work.

DOUGLAS, A. G., DOURAGHI-ZADEH, K., EGLINTON, G. (1969) The Fatty Acids of the alga *Botryococcus braunii*. *Phytochem.* **8**, 285-293.

The orange resting stage was purified, the lipid extract hydrolysed and the methyl esters examined by gas/liquid chromatography. The extract was shown to contain a variety of monocarboxylic acids ranging from C_{14} to C_{30} with appreciable amounts of palmitic, oleic and octacosenic acids. The total fatty acids of the alga are in relatively small amounts. A "synthetic coorongite" derived from botryococcene "rubber" was shown to contain traces of various carboxylic acids.

DOUGLAS, A. G., EGLINTON, G., MAXWELL, J. R. (1969) The Hydrocarbons of Coorongite. *Geochim. cosmochim. Acta* **33**, 569-577.

A brief survey of the literature is given followed by experimental data on the composition of coorongite extracts. The hydrocarbon distribution ranged from C_{13} to C_{27} and consisted of alkanes, terminal alkenes and some aromatic constituents. The fatty acids ranged from n-C_{14} to n-C_{28} with marked even/odd preference and major components at n-C_{16}, n-C_{18}. The C_{18} isoprenoids contained phytane and pristane, but no botryococcenes. No n-alkanes were detected in the orange bloom state of *Botryococcus*. The paper shows that hydrocarbons amounted to 0.53% of the sample. As the extract amounted to 50% of the sample it is unfortunate that no attempt was made to characterise the whole extract.

DULHUNTY, J. A. (1944) Origin of the N.S.W. Torbanites. *Proc. Linn. Soc. N.S.W.* **69**, 26-48.

The section (p. 31) entitled "Coorongite and its relation to Torbanite" gives a short account of previous work and describes samples collected by the writer. Dulhunty defines coorongite as the "peat-stage" in the formation of torbanite and gives convincing reasons to support his argument. The properties of torbanite and coorongite are compared and discussed.

DYER, W. T. THISTLETON (1872) On a Substance Known as Australian Caoutchouc. *J. Bot., Lond.* **10**, 103-106.

This paper provides the first reliable description of coorongite. The paper states "It consists of sheet-like masses—more than one inch thick and is confined to a depressed portion of the district, the bottom of which is sandy and grass covered . . . or on the sides of island-like elevations". Dyer quotes examinations by various workers which revealed "a granular and cellular structure". The suggestion is put forward that it might be a cryptogamic plant but this is then discounted because of the inexplicably small amount of oxygen. Dyer states, prophetically, that coorongite "is practically a hydrocarbon" and that the origin of the substance is likely to cause a great controversy.

GELPI, E., ORÓ, J., SCHNEIDER, H. J. & BENNETT, E. O. (1968) Olefins of High Molecular Weight in Two Microscopic Algae. *Science, N.Y.* **161**, 700-702.

Laboratory cultures of *B. braunii* have been shown to contain alkenes with carbon numbers ranging from C_{17} to C_{33} with one, two and three double bonds. The C_{27}, C_{29} and C_{31} diolefins were predominant and hydrocarbon distribution was similar to that of the kerogen of certain oil shales.

DE HAUTPICK, E. (1923) Coorongite, A Petroleum Product. *Min. J., Lond.*, **142**, 575.

A short contribution discussing the origin, occurrence and properties of coorongite. The writer errs in dismissing its vegetal origin on the basis of growth. This paper illustrates the conceptual difficulties of early investigators who could not reconcile a "pure" hydrocarbon being produced by algae. Unsaponifiable oils were considered part of the mineral kingdom and therefore must indicate the possible presence of petroleum. His report to The Coorong Oil Company (14 pp., issued June 19, 1923 Adelaide) further elaborates on the alleged interconnection between coorongite and the occurrence of petroleum. De Hautpick urges further boring in the Coorong area.

DE HAUTPICK, E. (1926) Note sur le minéral bitumeneux dit "Coorongite" et sur son témoignage de la formation du pétrole. *Bull. Soc. géol. Fr.* **26**(4), 61-66.

The writer reviews previous work and mentions there are many previous papers including a bibliography by L. Wahtall (the present reviewer can find no record—R.F.C.). Mention is made that coorongite appears to have been transported from where it was formed. It is stated that the formation of this "migratory" mineral has been recorded only in 1865 and 1920, after heavy rain. The paper gives the physical properties of coorongite and notes that, on destructive distillation, the material yields a whole series of "petroleum" products, none of which are saponifiable to any extent. Although coorongite is of vegetative origin, de Hautpick reaches the conclusion that "here is the true source rocks of petroleum", i.e. oil globules inside vegetation. This paper again illustrates the enigma facing early workers who couldn't reconcile the nonsaponifiable "fats" of coorongite with its plant origin.

This is an important paper but it is particularly unfortunate that no literature references are provided. It might be mentioned, *inter alia*, that Captain Hautpick was associated with early share raising efforts in connection with coorongite and petroleum in South Australia.

HILLEN, L. W. (1976) Prospects for Liquid Hydrocarbon Fuels from Solar Energy via the Alga *Botryococcus braunii*. 47th ANZAAS Conference (Hobart) May 1976.

This paper reviews the occurrence of coorongite and states that there are four well documented areas on the coastal sandy lowlands of Australia where this deposit is found. A study of the growth of coorongite suggests that this alga has potentialities as an energy source, however, the large water areas required for commercial production would present difficulty in any large scale undertaking.

JACKSON, J. R. (1872) Coorongite or Mineral Caoutchouc of South Australia. *Pharm. J.* **31**, 763-4 & 785.

Portion of the paper is based on the earlier observations of Francis (1866—Suppl.) regarding the occurrence and probable nature of coorongite. Jackson found coorongite to be "resolvable into two educts: (1) soft semi-

fluid like balsam . . . , resembling vegetable wax, and (2) a tough pulverulent substance . . . (like) . . . a modified form of cellulose".

KNIGHTS, B. A., BROWN, A. C., CONWAY, E., & MIDDLEDITCH, B. S. (1970) Hydrocarbons from the Green Form of the Freshwater Alga *Botryococcus braunii*. *Phytochem*. **9**, 1317-1324.

Botryococcus braunii occurs in two distinct forms, the brown resting stage containing up to 70% of its dry weight of two isomeric hydrocarbons. The green exponential growth form is shown to contain about 20% diene hydrocarbons in the C_{27}-C_{31} range.
Ozonolysis, gas chromatography and mass spectral data showed that the diene compounds had the general formula

$$CH_2{:}CH.(CH_2)_n.CH{:}CH.(CH_2)_7.CH_3$$

where n = 17, 19, and 15, in order of abundance. The disubstituted double bond is *cis* form, in the same position as in oleic acid.

LITINSKY, L. L. (1921) Balkash "Sapropelite", *Petroleum* (Berlin) **17**, 437-440.

Sapropelite from Lake Balkash is a dark coloured substance alleged to be produced by the alga *B. braunii*. It burns with a sooty yellow flame with a peculiar odour. The newly formed sapropelite is green but quickly changes to a yellow brown viscous mass which can be cut by a knife. Organic solvents may be used to separate the material into a hard paraffinic wax-like substance which may amount to 42% of the raw material. Destructive distillation gives a series of hydrocarbon fractions. Even when kept for five years there is no change in its physical properties.

MAXWELL, J. R., DOUGLAS, A. G., EGLINTON, G., & MCCORMICK, A. (1968) The Botryococcenes—Hydrocarbons of Novel structure from the Alga *Botryococcus braunii* Kutzing. *Phytochem*. **7**, 2157-2171.

The nature, occurrence, and previous work on *B. braunii* are discussed. Early analyses showed a high lipid content containing a large amount of unsaponifiable matter. By the application of column chromatography, mass and infra-red spectroscopy it has been shown that the oily matter is not fatty ester as previously believed. The lipids consist largely of two polyene hydrocarbons of novel structure, which have been called botryococcene and isobotryococcene. The elemental composition corresponds to $C_{34}H_{58}$. Infra-red spectra show the presence of exomethylene and vinyl groups together with much unsaturation. High resolution spectroscopy indicate two terminal vinyl groups, six methyl groups, and perhaps four exomethylene groups. A suggested structure is put forward. The behaviour of the dead algal colonies and the formation of coorongite can well be explained in terms of these hydrocarbons.
The paper presents entirely new evidence on the composition of coorongite and marked the end of the Stadnikov/Cane fatty acid theory.

MAWSON, D. (1938) Further Discoveries of Sapropelic Deposits in The Coorong Region of South Australia. *Oil Shale and Cannel Coal*, 50-52 (Institute of Petroleum: London).

The geological and topological features of The Coorong area are given and observations made on the flora of the saline lagoons. It is stated that the locality is famous for the occurrence of coorongite. Apart from a useful discussion on the area's geology, little pertinent information is presented on coorongite.

MORGAN, R. J. (1921) The Occurence of Coorongite in Central Asia. *Chem. Engng. & Min. Rev*. 348, July 5, 1921.

This paper gives an interesting description of the balkashite area in Siberia. Balkashite is found in Lake Ala-Kool which is a saline extension of the fresh-water Lake Balkash. Coorongite (balkashite) occurs above and at the shore margin. It is a yellowish spongy material which burns with a smoky flame with a disagreeable odour. The deposits vary from 2 feet to 10 feet in width and from thin sheets up to 2" thick. Balkashite is always mixed with algal remains and other general sapropel. Morgan states that the alga grows prolifically at the margin of the lagoon but only in shallow water and preferably where there is some surface disturbance, such as that caused by breezes. He states that balkashite is never found in the main lake and it is interesting to note (R.F.C.) that coorongite has never been recorded as growing in The Coorong itself. Similar deposits have been observed in Turkestan and elsewhere in Siberia.

REDWOOD, B. (1907) Report on a Sample of N'hangellite from Inhambane, Portuguese East Africa. *Bull. Misc. Inf. R. bot. Gdns Kew* **5**, 151-153.

A short description of N'hangellite together with proximate analyses. Redwood showed that destructive distillation produced, in addition to an aqueous phase and coke, an oily product resembling mineral oil. The elemental analyses showed figures comparable to those of coorongite and that the two deposits are similar products of the same origin.

SIMPSON, E. S. (1926) Coorongite. *Rep. Dep. Mines, West. Aust.* 234-235.

Coorongite has been found in many localities near the South Coast of Western Australia. Sheets of coorongite, up to one inch thick, have been gathered from a swamp at Martagallup. Dr Simpson, the government analyst, dismisses any connection between the occurrences of coorongite and petroleum. He points out that oily liquids can be obtained by the distillation of "almost any organic substance from coal to cucumbers".

STADNIKOV, G. L., & WEIZMANN, A. O. (1929) Transformation of Fatty Acids During Geological Periods III. *Brennst.-Chem.* **10**, 401-403.

Extracts of boghead coal were shown to consist mainly of polymers of unsaturated fatty acids. Such fatty acids are shown to be the parent substances of both coorongite and balkashite. Analysis has shown that coorongite has a high content of saponifiable and unsaponifiable organic acids. Polymerisation in coorongite is not extensive enough to make it totally insoluble.

STADNIKOV, G. L. (1930) Die Entstehung von Kohle und Erdöl—Die Umwandlung der organischen Substanz im Laufe der geologischen Zeitperioden. *Schr. Geb. Brennstoffgeol.* 254 pp. (Enke: Stuttgart).

Sections of the book discuss the oxidation and polymerisation of fatty acids into rubber-like materials. The author outlines the role of coorongite and balkashite in the formation of boghead coal. Investigations show that balkashite is not a wax or of mineral origin but an algal byproduct (wrongly termed *Elaeophyton coorongiana*) derived from fatty matter. Coorongite is similar in constitution and both can be separated into soluble and insoluble portions. The solubles are a thick yellow oil whereas the residue is a rubbery solid. Stadnikov did a great deal of fundamental work showing that oxidation and polymerisation of unsaturated fatty acids could give rise to either rubbers or brittle solids. His hypothesis of the decarboxylation of an acid to yield hydrocarbons was well supported by existing evidence. Recent results, showing that hydrocarbons were the direct algal metabolites, were possible only after the perfection of vapour chromatography. Stadnikov ascribes somewhat different diagnetic routes to coorongite and balkashite depending on conditions of sedimentation and on the ratio of aerobic to anaerobic environments.

STADNIKOV, G. L., & VOZZHINSKA, Z. I. (1930) Transformation of Fatty Acids during Geological Periods IV. *Brennst.- Chem.* **11**, 414-416.

Balkashite, like coorongite is derived from *Botryococcus braunii* and the remnants of algae can be easily distinguished in samples of both deposits. Fresh balkashite oxidises in the atmosphere and undergoes a slow hardening process. Some fatty acids also show a great tendency to polymerise to insoluble rubber-like materials. Microscopic examination of bogheads and Moscow cannel coal also shows evidence of algal origin.

TEMPERLEY, B. N. (1936) *Botryococcus* and the Algal Coals. Part II. The Boghead Controversy and the Morphology of the Boghead Algae. *Trans. R. Soc. Edin.* **58**(3), 855-868.

The second part of this paper (see Blackburn 1936) deals with the interrelationships between *Botryococcus braunii*, coorongite and torbanite. The morphology and mode of reproduction of the alga are discussed and illustrated with diagrams and photomicrographs. Temperley states that, in coorongite, the characteristic cup-in-cup structure has coalesced into a structureless rubbery mass. The important conclusions of this paper laid the groundwork for most later research on the phytochemistry of algal oil shales and showed that the "yellow bodies" of Scottish boghead and the torbanite of N.S.W. were, in fact, remains of *Botryococcus*. The paper also discusses the vegetal origin of coorongite and its close relationship with balkashite.

THIESSEN, R. (1925) Origin of Boghead Coals. *Prof. Pap. U.S. geol. Surv.* **132**, 121-135.

This publication deals largely with the origin of the kerogen of bogheads and torbanites. A section (pp. 127-130) is specifically devoted to coorongite, its history, occurrence and composition. Thiessen failed to recognise the genus but applied a new name of *Elaeophyton coorongiana*. Samples from The Coorong were examined and described. Data on the chemical properties of coorongite are given including elemental and proximate analyses. Thiessen believed that it was the oil in the cell wall of the living plant which provides the "yellow bodies" of boghead coal and the matrix of coorongite.

TRAVERSE, A. (1955) Occurrence of the Oil Forming Alga *Botryococcus* in Lignites and other Tertiary Sediments. *Micropal.* **1**, 343-350.

Although balkashite and coorongite receive only a mention, the paper presents a good review of (the ubiquity) of the occurrence of

Botryococcus and its role in organic rich deposits. Traverse pre-empts the later discovery that the alga itself may give rise to hydrocarbons. The author also states that other fossil genera described in the literature are often varieties of *Botryococcus* and that it ocurs in a wide variety of geological ages and geographical situations.

WARD, L. K. (1913) The possibilities of the Discovery of Petroleum on Kangaroo Island and the Western Coast of Eyre's Peninsula. *Bull. geol. Surv. S. Aust.* **2**, 15-20.

The history of coorongite is given and previous investigations are discussed. The opinion is put forward that coorongite is not a petroleum product and analyses would indicate a hydrocarbon-like material of unsaturated nature. Coorongite occurs on the northwestern shore of Murrays Lagoon on Kangaroo Island where a scum is to be found on banks below flood level. The deposits are associated with much vegetal detritus. It is believed that coorongite might be an oxidized product of "some pre-existing hydrocarbon". At the time of publication, this paper was the best general survey and the references are nearly complete. A bibliography is given.

WARD, L. K. (1915) The Supposed Oil Bearing Areas of South Australia. *Bull. geol. Surv. S. Aust.* **4**, 36-37.

Section 3 of this publication discusses the alleged connection between coorongite and petroleum. Coorongite is found on the shores of Murrays Lagoon (Kangaroo Island) and close to the Coorong area. It is found a "few feet down on old shores on which sand and debris has subsequently collected" or at the surface on banks associated with ponds after wet seasons. The paper gives a good description of the occurrence of coorongite and asserts that all facts predicate against its being associated with petroleum seepages.
The opinion is put forward that coorongite originates from lowly vegetable organisms which grow on the lagoons and that it has a genesis similar to N'hangellite (see ref. Boodle, 1907).

WARD, L. K. (1916) A Review of Mining Operations in the State of South Australia, Issue No. 24, p. 43, Department of Mines (Govt Printer: Adelaide).

The report emphasises the falsehood of associating coorongite with the occurrence of petroleum. The report goes on to state that pieces of coorongite which were placed "on the crests of calcareous sand dunes . . . . (was) regarded as evidence that the material was deliberately placed there with fraudulent intent".

WARD, L. K. (1944) Search for Oil in South Australia. *Bull. geol. Surv. S. Aust.* **22**.

There is a short reference to coorongite (p. 12) in the discussion of the occurrence of petroleum in South Australia. A review is given (p. 17) of the prospecting boreholes which were put down in The Coorong in the belief of the association between mineral oil and coorongite.

WILSON, R. C. (1926) Reported oil at Kenderup. *Rep. Dep. Mines West. Aust.*, p. 78.

Mr. Wilson visited Lake Martagallup at the request of local residents and collected pieces of coorongite "about the size of dinner plates" at the edges of the lake from shorelines which have now dried up.

ZALESSKY, M. D. (1914) On the Nature of *Pila*, the Yellow Bodies of Boghead and on Sapropel of the Ala-Kool of Lake Balkash. *Bull. Comité Géol. St Petersbourg* **33**(248), 495-507.

The paper supports the opinion that the "yellow bodies" of bogheads were not algal in origin but highly sculptured walls of the spores of cryptogams. At that time there was confusion between the genus *Pila* and the alga of balkashite. Zalessky records that, along the Ala-Kool, this alga comes to the surface of the water and it contains a considerable amount of oil. Decomposition of the alga on the shores of the lake generates much hydrogen sulphide while the green plant residue changes to a brownish rubber-like mass.

ZALESSKY, M. D. (1917) On Some Sapropelic Fossils. *C. r. & Bull. Soc. géol. Fr.* 4th Series, **17**, 373-379.

Because of further work, Zalessky believed that Estonian kukkersite is an oil shale derived from *Botryococcus*. This alga is similar to that found growing in Lakes Bieloe and Kolomenskoe in the Tver district of Siberia. The sapropelite is also found in the Ala-Kool gulf of Lake Balkash. In Lake Bieloe, areas up to nine metres square are covered with a type of rubber humic jelly. This sapropel has been used as a source of ammonia for agricultural applications. Other more mature forms of the sapropelite are found in the Kamenkarita valleys in Siberia and known as Kouswvriaslo.

ZALESSKY, M. D. (1926) Sur les nouvelles Algues découvertes dans le Sapropélogène du Lac Beloe et sur une Algue sapropélogène. *Revue gén. Bot.* **38**, 31-42.

A description is given of the deposits at Lake Balkash. The deposits are formed by the coalescence of vast numbers of the colonial alga *B. braunii*, which later dry on the shores of the lake. The deposits are very thick and resist decay. Zalessky gives a description of the variety of *Botryococcus* inhabiting the Siberian lakes. Zalessky shows that the alga has various forms depending on the ecological and environmental conditions.

Supplementary chronological bibliography

Although not always of scientific merit, early references to the heated controversy over the origin of coorongite are included in this survey. The violent arguments arose because of difference of opinion as to whether coorongite was of mineral or of plant origin. If the former, it was alleged that the discovery of a large petroleum deposit could not be discounted. If, on the other hand, the substance was a vegetative growth, then it was said it should be possible to cultivate the plant and harvest the "oil". It is interesting to note that this latter possibility has been recently put forward (Hillen 1976).

As it proved difficult to ascertain the author of some newspaper articles, a selection of the main contributions is set down in chronological order.

FRANCIS, G. (1866) The Substance found near The Coorong. *The S. Aust. Register* 8.5.66.

This well presented letter (p. 3, col. 3) gives a general description of coorongite including a reliable examination of its physical properties and chemical reactions. Francis states that all evidence points to a vegetative origin as, under the microscope, coorongite has a cellular structure. Francis considers it "to be neither caoutchouc, elastic bitumen, asphalt or petroleum but a peculiar fungoid growth and that it has no connection with coal or any other combustible mineral". The information in this early article is remarkably true and, although no quantitative data are provided, the qualitative observations are largely still valid. The writer suggests that the substance probably has some financial value if sufficient quantity were available.

MUECKE (1869a) *The Adelaide Observer* 3.7.69.

A letter (p. 6, col. 7) decrying any possibility of a connection between coorongite and petroleum. Dr Muecke stated that coorongite has been found on the top of recent sands and shelly limestones and that it never had any connection with the underlying strata. He suggested that coorongite arose from allies of the the grass trees because of its resinous and inflammable nature. "The damp yellow juice exudes from the knot and bottom stalks during the summer heat and flows on the sand where it becomes hard, as every caoutchouc does."

MUECKE (1869b) Caoutchouc. *The S. Aust. Register* 31.7.69.

A further letter (p. 3, col. 8) in reply to another letter reaffirming his opinion on the vegetal origin of coorongite and stating that, under no circumstances, can coorongite be regarded as of mineral origin—see also The Adelaide Observer 7.8.69 (p. 13, col. 5).

ANON (1871) *The S. Aust. Register* 29.8.71.

The article (p. 2, col. 4) contains reproductions of letters from J. Hooker of Kew Gardens and from M. J. Berkeley regarding a substance called "mineral gamboge" which is believed to be a "collemal" in an imperfect state. The general opinion was that the material (coorongite) is of vegetal origin but no firm views are given.

ANON (1871) A Singular Vegetable Formation. *The Advertiser* 29.8.71.

An article (p. 2, col. 5) concerning the dichotomy of opinion on the origin of coorongite, pointing out that a "good deal of money" had been spent in the belief that "mineral gamboge" was an indication of petroleum. Samples had been sent to Kew Gardens and examined by M. J. Berkeley. Berkeley's opinion was that the substance (coorongite) was "a collemal in an imperfect state and a thin slice shows necklaces of gonidia". The famous Dr Hooker, who had written to Adelaide "sets the matter at rest", i.e. coorongite belonged to the vegetable kingdom.

A similar article also appears in *The S. Aust. Register* of 29.8.1871 (see above).

F.V. (Initials only) (1871) Coorongite—Vegetable or Not? *S. Aust. Express & Telegraph* 1.9.71.

A letter (p. 3, col. 1) in reply to the previous abstract. F.V. affirms that the descriptions given can only be applied to globules of mineral oil which are dispersed in water. "The evidence is conclusive that fixed petroleum oil floating on water . . . forms a coat of varnish or gum more or less thick according to the accidents of position". F.V. appears as a strong adherant of the "mineral oil" theory. This letter also appears in *The Adelaide Observer* of 1.9.1871 (p. 3).

WHITTELL, H. A. (1871) *The Adelaide Observer* 30.9.71.

A reply to the previous reference, which agrees that coorongite has an organic structure, but, stating that microscope thin section views cannot be explained in terms of the plant origin suggested by M. J. Berkeley. Further, any suggestion of coorongite being a lichen is dismissed on account of the occurrence of diatoms embedded in the matrix.

SCRUTTON, T. U. (1874) Petroleum or Coal in S. Aust. *The S. Aust. Chronicle & Weekly Mail* Suppl. to issue of 21.2.74.

This article reports an address by T. U. Scrutton (p. 1, cols 1-4) to the S.A. Chamber of Manufacturers extolling the many virtues of petroleum whilst calling for further investments in oil drilling. Scrutton refers to the value of coorongite (which he confuses with elaterite) and completely dismisses any possibility of its plant origin. He states that, because of the high oil yield from coorongite on heating, it is likely that, in the past, "millions of tons of oil have been projected from subterranean sources" and it only needs money to find it. Many aspects of the report had no substantial basis at the time, and subsequent efforts have shown that they were erroneous. Nevertheless, some interesting information on the early discovery of coorongite is given as well as descriptions of the area. The address by Mr Scrutton was also reported in *The South Australian Register* of 16.2.74 (pp. 5 and 6). The report was also issued as a separate pamhplet under the same title.

BASEDOW, H. (1925) *The Adelaide Observer* 14.8.25.

A contribution stating that authorities in the United States had confirmed that coorongite "consists in part of vegetable organism which is oil bearing". Basedow explains that he had grown the alga under laboratory conditions and "the little plants developed so plentifully that the material grew up the sides and neck of the bottle . . . If this can be done on a small scale, why not apply it to the large?" He further states that the material "could be as valuable to the State as a gusher of liquid oil" but no one seems to have given credence to his suggestion.

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